Development of High-Energy Lithium-Sulfur Batteries

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Project ID#: bat282

Overview

Timeline
- Start date: Oct. 2021
- End date: Sept. 2024
- Percent complete: 25%

Barriers
- Limited cycle life at high energy
- Low volumetric energy density
- Shuttling effect and self-discharge
- Low sulfur (S) utilization rate at high S loading

Budget
- Total project funding: $900k
- DOE share: 100%
- Funding received in FY22: $300k

Partners
- Brookhaven National Laboratory
- Thermo Fisher Scientific
- Energy Storage Materials Initiative (ESMI)/PNNL

Relevance/Objectives

- Advance fundamental understandings and development of materials and electrodes to improve S utilization and cycle life at practical high S loading and lean electrolyte conditions.
- Rationalize low-porosity S electrode design to save more electrolyte for extending cell life.
- Provide S cathode materials and electrodes to support Battery500 Li-S pouch cell.
- Project efforts are directly aimed at key barriers of low practical energy density, shuttling effect, and limited cycling life of realistic Li-S batteries.

Milestones

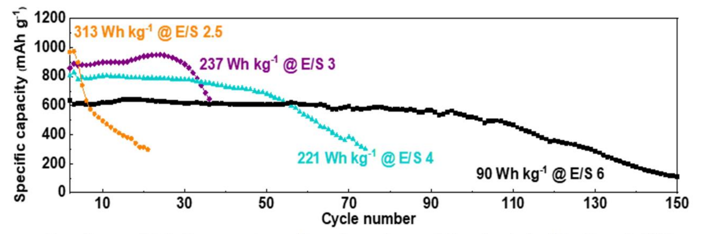
Date	Milestones and Go/No-Go Decisions	Status
December 2021	Build 3D electrode models to simulate electrolyte transport and S reactions in high-loading and low-porosity electrodes.	Completed
March 2022	Optimize S/C material and electrode architecture to realize S utilization >1100 mAh/g in high loading electrode (>4 mg S/cm^2) with S content >70% and porosity <35%.	Completed
June 2022	Study impacts of electrode architecture and topography on S reactions and cell cycling.	On track
September 2022	Processing of high-loading (>4 mg/cm^2) and dense (<35% porosity) S electrodes at a relevant scale for pouch cell fabrication.	On track

Approach/Strategy

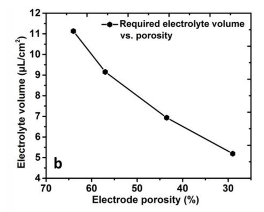
- Build 3D electrode model to simulate the impacts of material property/electrode architecture on electrode wetting, Li-polysulfide migration, and S reaction kinetics.
- Develop a single-particle-layer electrode (SPLE) approach to realize high specific capacity in high-loading and low-porosity S electrode.
- Study the effects of electrode architecture on cell performance at practical conditions by using electrochemical and advanced characterization tools.
- Integrate polymer solid Li$^+$ conductors into electrode to enhance durability of Li$^+$ conduction network, extending cell life and suppressing Li-polysulfide shuttling.

Technical Accomplishments

Limiting factor of long-life Li-S cells: "accessible" electrolyte



- Cycling of Li-S pouch cells at various Electrolyte/Sulfur (E/S) ratio (S > 4 mg/cm^2; 50 µm Li foil;1M LiTFSI/DOL/DME+0.3 M $LiNO_3$). *Collaboration with Battery500 pouch cell team.*

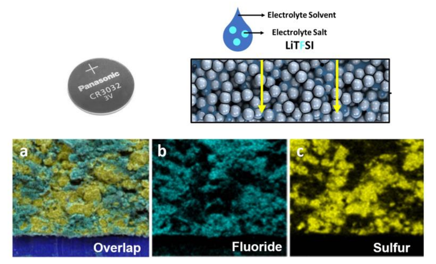


- Electrolyte required for pore filling at different electrode porosities (S loading, 4 mg/cm^2).

- The amount of Li "accessible" electrolyte determines the cycle life of Li-S cells.
- High porosity of S electrode "wastes" a big proportion of electrolyte.
- It is crucial to balance the electrolyte distribution for both cathode wetting (inside of cathode) and Li cycling (outside of cathode).

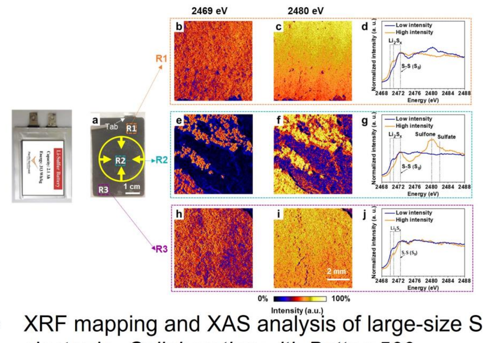
Electrolyte wetting issues in high-loading and low-porosity S electrode

Nonuniform electrolyte wetting along **vertical** direction



- Cross-sectional SEM-EDS of S electrode after electrolyte injection

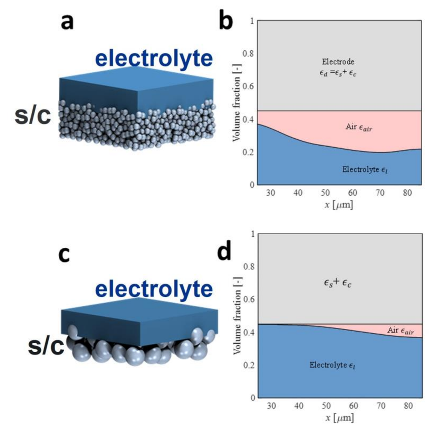
Nonuniform electrolyte wetting along **planar** direction



- XRF mapping and XAS analysis of large-size S electrode. *Collaboration with Battery500*

- Electrolyte wetting issues exist along both vertical and planar directions of electrode film.
- Direct reduction of porosity exaggerates such wetting issues.
- Need electrode with low tortuosity along both vertical and planar directions.

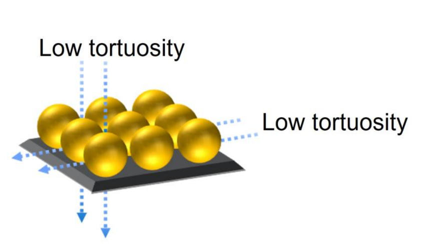
Rationalized material design for low-porosity S electrode



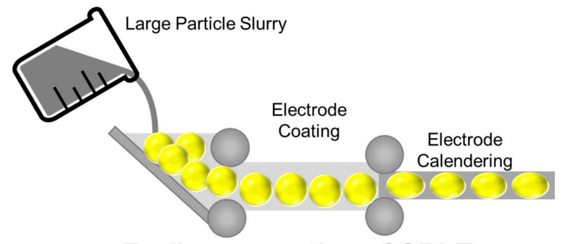
- Electrolyte wetting in S electrode was simulated and correlated to the cathode particle size (a, b: large particle cathode (LPC); c,d : small particle cathode (SPC)).
- The surface property and trapped air affect electrolyte wetting.
- Electrode with large secondary particles has better wettability compared with the small particle electrode.

In collaboration with Drs. Jie Bao, Zhijie Xu at PNNL

Rationalized low-porosity cathode architecture: single-particle-layer electrode (SPLE)



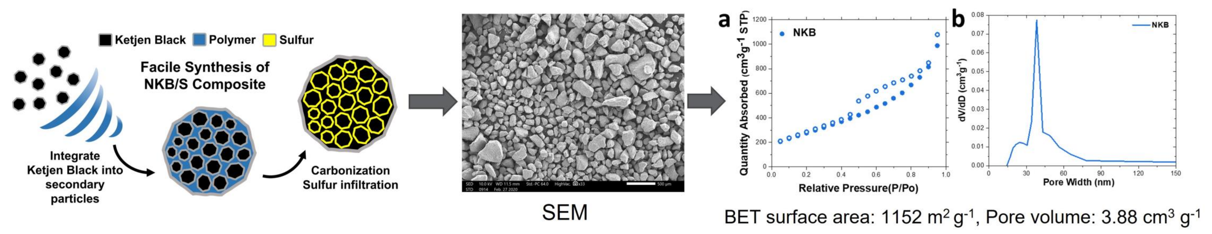
- Low-tortuosity 3D channels



- Facile preparation of SPLE

- The SPLE structure would enhance both vertical electrode wetting of thick electrode and planar electrolyte transport in large-area electrode.

Large S/C particles with sufficient surface area and pore volume for SPLE

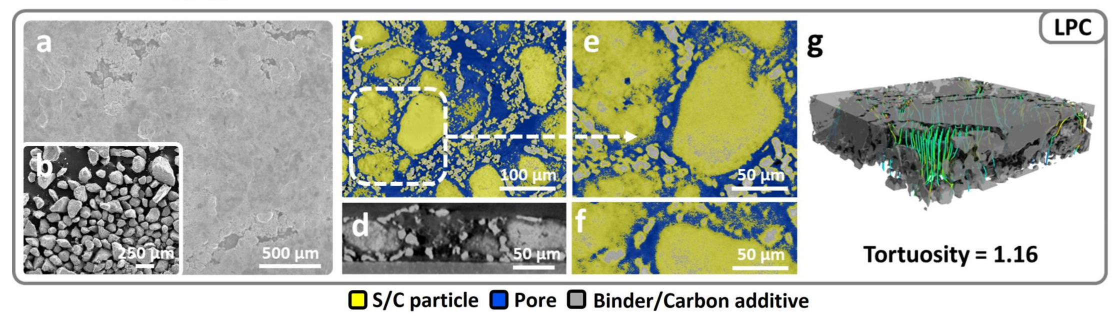


BET surface area: 1152 m^2 g^{-1}, Pore volume: 3.88 cm^3 g^{-1}

- NKB/S (~80% S) particles were synthesized and scaled up for pouch cell fabrication

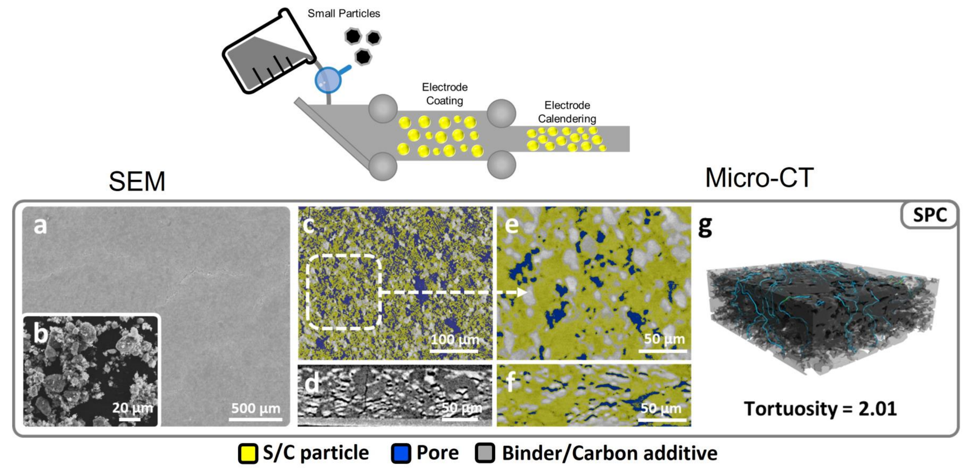
- Materials (NKB) can be easily prepared with controllable particle size.
- Scaling-up synthesis of NKB/S for Battery500 pouch cell team.

Verified low-tortuosity in SPLE



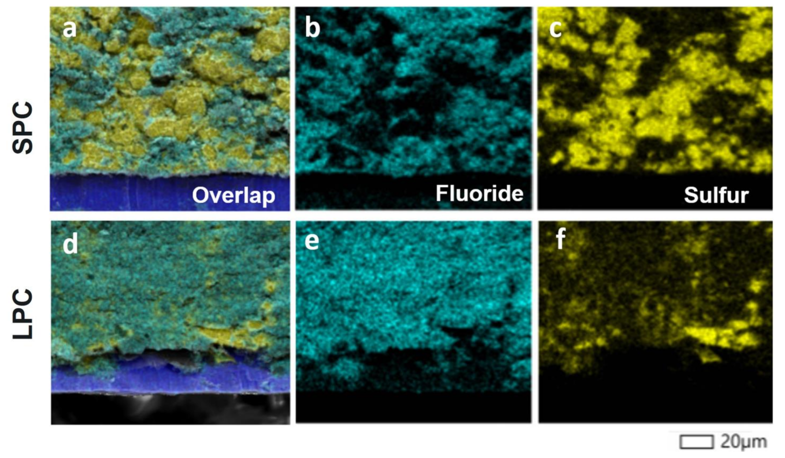
- Confirmed SPLE structure by Micro-CT.
- The SPLE has a low tortuosity electrode of 1.16 at 45% porosity, helpful for electrolyte wetting.

High-tortuosity multiple-particle-layer electrode (MPLE)



- Using small particles results in a multiple-particle-layer electrode architecture, which has a high electrode tortuosity of 2.01 at a 45% porosity.

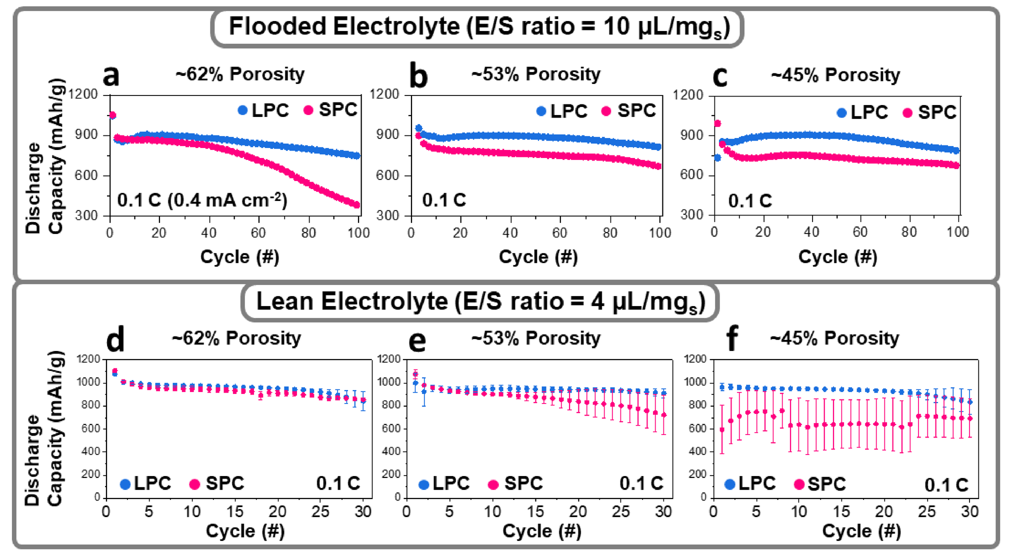
Improved electrolyte wetting in low-porosity SPLE



- Cross-sectional SEM-EDS of small particle cathode (SPC) and large particle cathode (LPC).

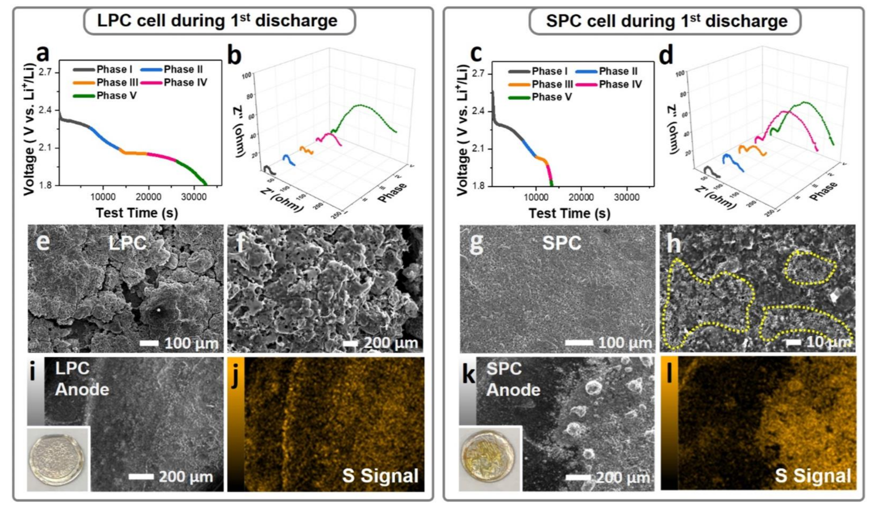
- Compared with SPC, LPC has more uniform F signal (from LiTFSI of electrolyte), indicating better electrolyte wetting.

Improved cell performance of LPC vs. SPC



- Compared with SPC, LPC has higher specific capacity and better cycling stability, especially at low porosity and lean electrolyte conditions.

Different reaction pathways in SPC and LPC at E/S=4



S loading: 4 mg$_s$ cm^{-2}; S content: 64%; E/S ratio: 4 µL mg$_s^{-1}$; Porosity: ~45%; Thickness: 60 µm

- The poor electrolyte wetting in SPC leads to high cell resistance and early surface passivation as a result of Li_2S accumulation.
- The LPC shows a suppressed shuttling effect due to the large dimensions the of SPC particles.

Collaboration and Coordination with Other Institutes

- Brookhaven National Laboratory: reaction mechanism study
- Thermo Fisher Scientific: electrode characterization
- ESMI/PNNL: electrode-level simulation
- Environmental Molecular Sciences Laboratory (EMSL)/PNNL: material/electrode characterization

Remaining Challenges and Barriers

- Short cycle life at both high-loading S cathodes and lean electrolyte conditions
- Loss of electrolyte in cell dead volume
- Depletion of electrolyte/additives
- Instability of Li metal anode

Future Work - FY2022

- Continue to understand material and electrode challenges by using experimental and theoretical simulation tools.
- Save liquid electrolyte from pore filling to extending cell life.
- Eliminate Li-polysulfide free migration and reduce its interference on Li anode.
- Improve processibility of low-porosity S cathode at relevant scale for pouch cell fabrication.

Any proposed future work is subject to change based on funding levels

Summary

1. Electrolyte wetting issue in low-porosity S electrodes was studied by experimental characterization and theoretical simulation.
2. A single-particle-layer electrode (SPLE) approach was proposed and validated for low tortuosity electrode fabrication.
3. The SPLE composed of large-size integrated KB (IKB) particles shows better electrolyte wetting and lower polysulfide shuttling, improving both S specific capacity and cycling stability.
4. By controlling electrode structure, high-mass-loading S electrodes (>4 mg cm^{-2}) with low porosity of ~35% can deliver a high S utilization rate (>1100 mAh g^{-1}) at very lean electrolyte conditions (E/S=3 µL mg^{-1}).
5. The large-size IKB materials were scaled-up synthesized and transferred to Battery500 for pouch cell fabrication.

Acknowledgments

- Support from the DOE/OVT/BMR program is greatly appreciated
- Team Members: Shuo Feng, Lili Shi, Cassidy Anderson, Phung Le, Ji-Guang Zhang and Jie Xiao